TITLE: MECHANISTIC STUDIES AND DESIGN OF HIGHLY ACTIVE CUPRATE CATALYSTS FOR THE DIRECT DECOMPOSITION AND SELECTIVE REDUCTION OF NITRIC OXIDE AND HYDROCARBONS TO NITROGEN FOR ABATEMENT OF STACK EMISSIONS

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ABSTRACT

OBJECTIVE

The original objective of this project was to explore mechanistic aspects of the decomposition, oxidation, and selective oxidation of nitric oxide (NO) over different cuprate catalysts, in order to design better catalysts for the NO_x control from stationary and mobile power sources. Previous experiments had suggested that these cuprate catalysts were promising.

In the meantime, however, we found that one of our newly developed and completely novel supported molten metal catalysts (SMMC), namely liquid indium supported on controlled pore glass (abbreviated as In-CPG-SMMC), provided superior catalytic activity and stability for the SCR of NO by ethanol, under net oxidizing conditions, in the presence and absence of water vapors, and at high gas hourly space velocities (GHSVs). It was, therefore, decided to instead pursue this even more attractive new catalyst for the NO_x treatment.

SIGNIFICANCE OF PROJECT

Abatement of stack emissions from coal combustion is essential for the retention of clean air while utilizing the substantial coal reserves. Further, although lean burn or diesel engines are characterized by lower fuel consumption and CO_2 emissions than engines operating at the stoichiometric air/fuel ratio, the presence of oxygen in their emissions precludes the use of the current "three-way" type catalysts. The state-of-the-art technology for NO removal from stationary sources involves the use of ammonia as the selective reductant with platinum, vanadium pentoxide, or zeolite containing catalyst, but this technique suffers from some

limitations such as the maintenance of a sophisticated injector system, and the venting of any unreacted ammonia. For automobiles, of course, this is not viable, and the most promising technology so far is the use of hydrocarbon reductants with Cu-HZSM5 type catalysts. However, the activity of these catalysts drops significantly at higher temperatures and the presence of water vapors, which are unavoidable in combustion exhausts. Thus, developing a commercially usable catalyst with good hydrothermal stability for NO abatement emissions from both motor vehicles and stationary sources remains an important goal.

ACCOMPLISHMENTS TO DATE

We have previously reported the excellent performance of the In-CPG-SMMC catalyst, especially in the presence of water and at higher temperatures. In the past year, some of the fundamental aspects related to the supported molten indium catalysts have been further clarified. The dispersion of indium on the controlled pore glass has been measured using the volumetric method. Since indium is a non transition, weakly-chemisorbing metal, the choice of adsorbate gas was oxygen. Thus, chemisorption isotherms with oxygen were obtained at different temperatures both above and below the melting point of indium. In the pressure range covered, for all temperatures, the data obtained conform well to Freundlich type isotherms. With the amount of oxygen adsorbed for monolayer coverage thus obtained, together with the assumed stoichiometry of one oxygen atom per indium atom (i.e., O_2 adsorbs dissociativelly) the dispersion of indium on the support could be calculated as a function of catalyst loading.

The limits of applicability of the supported indium catalysts for the SCR process were tested by varying the gas hourly space velocities (GHSV), and by studying their tolerance towards SO_2 poisoning. As expected, conversions of NO to N_2 decreased as the GHSV increased. The addition of 30 ppm SO_2 into the reaction gas mixture caused a slight decrease of NO conversion to N_2. However, the NO conversion was restored to about 97 % of the SO_2 – free value, when the SO_2 was removed from the feed. Thus, SO_2 is merely a reversible reaction inhibitor, and not an irreversible catalyst poison.

Detailed kinetic studies, as well as adsorption measurements using a tapered element oscillating microbalance (TEOM®), were performed in order elucidate the SCR mechanism over this new catalyst. The reaction rate measurements were done at three different temperatures, three different GHSV, and at different partial pressures of NO, ethanol, and oxygen in the feed. Total NO conversions were maintained below 20 % to approximate differential reactor conditions. The alternate mechanisms of reaction were derived using the approach of reaction routes, coupled with the Langmuir-Hinshelwood-Hougen-Watson (LHHW) formalism involving a rate determining step to derive the corresponding rate expressions. The resulting rate expressions were fitted to experimental data utilizing the commercially available program Scientist® by MicroMath® Scientific Software. Subsequently all the parameters were optimized at the same time for a constant temperature using the least square method. The values of R^2 were above 0.93 for all temperatures. This work along with FTIR experiments is in progress to determine the mechanism and kinetics of the process.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles

- Serban, M., Halasz, I., Datta, R., “New Water Tolerant Supported Molten Metal Catalysts (SMMC) for the Selective Catalytic Reduction of Nitric Oxide by Ethanol”, *Cat.Lett*., **63** (1999) 217.

- Halasz, I., Serban, M., Datta, R., “Efficient Reduction of Nitric Oxide by Alcohols in the Presence of Excess Oxygen and Water over a New Indium on Controlled Pore Glass Supported Molten Metal Catalyst (In-CPG-SMMC)”, *Appl.Catal.B:Env*., submitted.

Conference Presentations

- Serban, M., Halasz, I., Datta, R., “New Water Tolerant Supported Molten Metal Catalysts (SMMC) for the Selective Catalytic Reduction of Nitric Oxide by Ethanol,” presented at *AIChE* Conference, Miami 1998.

- Serban, M., Datta, R., “Selective Catalytic Reduction of NO by Ethanol over Indium Supported on Controlled Pore Glass,” presented at the *New England Catalysis Society Conference*, Worcester 1999.

- Serban, M., Fishtik, I., Datta, R., “Kinetics and Mechanism of NO Selective Catalytic Reduction over Highly Active Novel Supported Molten Indium Catalyst,” presented at the *16th North American Meeting of the Catalysis Society Conference*, Boston 1999.

- Serban,M., Fishtik, I., Datta, R., “On the Use of Unity Bond Index-Quadratic Exponential Potential (UBI – QEP) Method in the Kinetic Modeling of the Selective Catalytic Reduction of NO by Ethanol,” presented at *AIChE* Conference, Dallas 1999.

- Serban,M., Fishtik, I., Datta, R., “Kinetics and Mechanism of Nitrogen Oxide Selective Catalytic Reduction (NO SCR) with Ethanol over Molten Indium on Controlled Pore Glass (In-CPG-SMMC)”, to be presented at *AIChE* Conference, Los Angeles 2000.

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- Manuela Serban, graduate (Ph.D.) student in chemical engineering, WPI.